



Relative basicities of cyclic ethers and esters. Chemistry of importance to ring-opening co- and terpolymerization reactions

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This manuscript is dedicated to the memory of Professor Michelle Millar, a good friend, superb synthetic chemist, and tireless contributor to the inorganic chemistry community.

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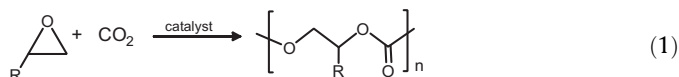
ABSTRACT

We have re-evaluated the use of the red-shifted ν_{OD} vibrational mode in CH_3OD as a result of hydrogen-bonding to various oxygen donor ligands in determining the basicity strengths of such donors. This was accomplished by initially defining the relationship of the analogous vibrational shifts of several amines with respect to the corresponding shift in benzene versus their well-established $\text{p}K_b$ s in water. The reactivity ratios for terpolymerization processes involving two different epoxides and CO_2 catalyzed by binary (salen)MX/onium salt ($M = \text{Cr}$ or Co) catalyst systems were determined by a Fineman–Ross analysis, i.e., quantifying the amount of respective monomers in the polymer versus that in the feed during the early stages of the process. These reactivity ratios reflect the tendencies for an epoxide monomer to self-propagate or cross-propagate during the monomer enchainment process. The relative basicities of cyclic ethers were shown to greatly influence the interpretation of these measured reactivity ratios.

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1. Introduction

In endeavors to maintain a sustainable chemical industry, alternative feedstocks are needed to replace decreasing petroleum supplies. The utilization of carbon dioxide as a source of chemical carbon can contribute to meeting this shortage [1]. Among the processes exhibiting commercial viability are the incorporation of carbon dioxide into polymeric materials, a subject of much current interest [2]. Important among these processes is the completely alternating copolymerization of CO_2 and epoxides to provide polycarbonates (Eq. (1)) [3]. Because there are a limited number of epoxides which provide good selectivity for copolymer formation, it may be necessary to synthesize terpolymers from two such epoxide monomers and carbon dioxide in order to obtain polycarbonates with desirable physical properties.



The basicity of the cyclic ether should be a factor in the copolymerization of carbon dioxide with this monomer. That is, cyclic ether activation via binding to the metal center should correlate with the basicity of the cyclic ether in the absence of steric hindrance, and hence facilitates ring-opening by nucleophiles (Scheme 1). At sufficiently high CO_2 concentration, insertion of

CO_2 into the resulting metal alkoxide species is generally not rate-limiting. Hence, following the initiation step the rate of copolymerization should be both a function of the basicity of the cyclic ether monomer and the nucleophilicity of the growing polymer chain. The growing carbonate polymer chain in **3** serves as the recurring nucleophile in species **1**.

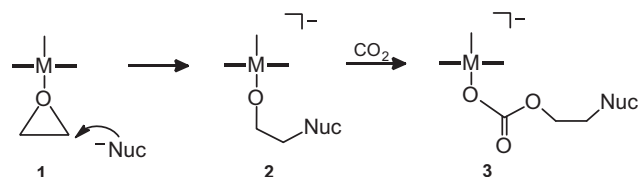
Fineman and Ross have defined a linear method for determining the monomer reactivity ratios for two monomers in a copolymerization reaction at low conversion by way of Eq. (2) [4]. M_1 and M_2 refer to the monomer composition in the feed and m_1 and m_2 to the monomer composition in the polymer. The monomer reactivity ratios are given by r_1 and r_2 , which are k_{11}/k_{12} and k_{22}/k_{21} in Scheme 2, respectively.

$$\frac{dM_1}{dM_2} = \frac{M_1 r_1 M_1 + M_2}{M_2 M_1 + r_2 M_2} = \frac{m_1}{m_2} \quad (2)$$

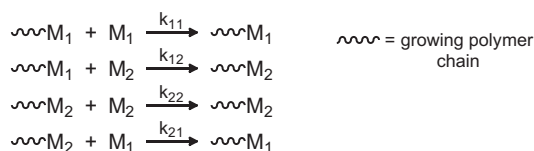
Upon examining the relative reactivity of two different cyclic ethers which differ significantly in basicities, the terpolymerization parameters should include both the rate constants for ring-opening and the binding constants for the monomers (Scheme 3) [5]. The binding constants in turn are proportional to the basicities of the cyclic ethers. Therefore, $r_1 = k_{11}K_{11}/k_{12}K_{12}$ and $r_2 = k_{22}K_{22}/k_{21}K_{21}$. In the absence of steric hindrance, if the K_b s of the two monomers are similar, K_{11} and K_{12} should be similar, and the reactivity ratio reduces to simply k_{11}/k_{12} . Hence, it is important to know the relative basicities of the two monomers involved in the polymerization process. The similarity of the values K_{11} and K_{21} , and K_{22} and K_{12} is a consequence of the polymer chains being essentially dissociated

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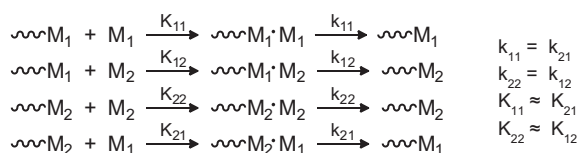
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Scheme 1.



Scheme 2.



Scheme 3.

from the metal center during the enchainment of the incoming epoxide. That is, in Scheme 1 the anionic nucleophile represents the growing polymer chains ($\sim M_1$ and $\sim M_2$).

2. Experimental

2.1. Spectral measurements

A calibration curve was initially made by determining the ν_{OD} of stretching vibration in CD_3OH dissolved in ten different amines with pK_b values in water spanning the range 2.55–9.62. The difference between the value of ν_{OD} of CH_3OD in benzene, determined to be 2667.4 cm^{-1} , and the corresponding ν_{OD} value in the amines was measured and plotted versus the pK_b of the amine (see Table 1 and Fig. 2). As noted in Fig. 2, there is a rough correlation between $\Delta\nu_{OD}$ and the amine pK_b with a correlation coefficient (R^2) of 0.9469. Similarly, the shifts of the ν_{OD} vibration in CH_3OD dissolved in the respective cyclic ether ($\sim 0.2\text{ M}$) and that in benzene were determined. From these shifts and the calibration curve pK_b values of the cyclic ethers were determined.

2.2. Terpolymerization reactions of styrene oxide/propylene oxide and CO_2

(S,S)-N,N'-bis(3,5-di-tert-butylsalicylidine)-1,2-cyclohexanediaminocobalt(III)-2,4-dinitrophenoxide (20.67 mg, 0.02627 mmol), bis(triphenylphosphine)iminium 2,4-dinitrophenoxide (18.96 mg, 0.02627 mmol), styrene oxide (2.00 mL, 17.5 mmol) and propylene oxide (3.00 mL, 42.9 mmol) were added to a 12 mL autoclave reactor which had previously been dried for 6 h. For other terpolymerization with different SO/PO ratio, the SO and PO volume were varied to maintain the total volume at 5 mL. The reactor was pressurized to 2 MPa with CO_2 and maintained at ambient temperature. Subsequent to the allotted time, the reactor was depressurized and a small aliquot was taken to be analyzed by 1H NMR to calculate the conversion of styrene oxide and propylene oxide. The reaction solution was dissolved in CH_2Cl_2 and added to c.a. 1 M HCl methanol solution to obtain pure polymer, which was dried *in vacuo* at $40\text{ }^\circ\text{C}$ and analyzed by 1H NMR.

3. Results and discussion

3.1. Determination of pK_b s of cyclic ethers

Over 70 years ago, Gordy and coworker established an empirical relationship between the K_b and the shift of the OD stretching vibration in methanol- d_1 dissolved in organic bases (Eq. (3)), where $\Delta\mu_{OD}$ = shifted value of ν_{OD} in microns from that in benzene [6–9]. Pertinent to the subject of terpolymerization processes involving two or more cyclic ethers and carbon dioxide, it is useful at this time to revisit the Gordy equation while extending it to relevant epoxides. Originally, these researchers established a correlation between the K_b of amines and the shift of ν_{OD} of CH_3OD in amines in comparison with that in benzene. The basicity constants were determined in aqueous solution and are interpreted as the ability of the base to attract a proton from water.

$$\Delta\mu_{OD} = 0.0147 \log K_b + 0.194 \quad (3)$$

In Fig. 1, we have re-plotted Gordy's original data in more commonly used units of cm^{-1} and pK_b , leading to Eq. (4) [8,9]. In an analogous manner, we have measured the shifts in the ν_{OD} vibration in CH_3OD dissolved in various amines and compiled that data in Table 1, along with the literature values of the pK_b of the amines determined in aqueous solutions [10–15]. These ν_{OD} s are compared to the corresponding value for CH_3OD in benzene of 2667.4 cm^{-1} . Our measurements result in the linear relationship (Fig. 2) which is slightly different from that of Gordy and coworker, Eq. (5). It should be noted that we utilized a high-resolution FTIR instrument, whereas, Gordy and coworker employed an infrared

Table 1
Infrared ν_{OD} shifts of methanol- d_1 in the presence of amines.

Amine	MeOD peak (cm^{-1})	OD band shift from benzene (cm^{-1}) ^a	pK_b	Ref. ^b
Piperidine	2422.5	−244.9	2.95	[10a]
Pyridine	2503.5	−163.9	8.79	[11]
Aniline	2509.3	−158.2	9.38	[12]
Tributylamine	2407.0	−260.4	3.11	[10b]
Trimethylaniline	2518.9	−148.5	9.62	[13]
Cyclohexylamine	2432.1	−235.3	3.36	[12]
4-Picoline	2507.3	−160.1	8.00	[14]
Triethylamine	2405.1	−262.3	3.35	[10b]
2,6-Lutidine	2464.9	−202.5	7.36	[14]
Diisopropylethylamine	2410.9	−256.5	2.55	[15]

^a ν_{OD} in benzene observed at 2667.4 cm^{-1} .

^b References are for best amine pK_b values in aqueous solution.

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